

2
BEST AVAILABLE COPY

10 Rec

10.1 JUL 2004

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

5001
(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
17 July 2003 (17.07.2003)

PCT

(10) International Publication Number
WO 03/058350 A1

(51) International Patent Classification⁷: **G03F 7/32**

[KR/KR]; 202-301 Dongsung-hyosung apt, Vision-2 dong, Pyongtaek-city 450-728 (KR). KANG, Doek-Man [KR/KR]; 108-402 Dong-A apt, Jamwon-dong 66-3, Seocho-gu, Seoul 137-948 (KR). CHOI, Kyung-Soo [KR/KR]; 227-34 Ojung-Dong, Daeduck-gu, Daejon 306-818 (KR).

(21) International Application Number: PCT/KR03/00030

(74) Agent: LEE, Byong-Ho; 5th Fl. Korea Reinsurance Bldg., 80 Soosong-dong, Chongro-ku, P.O.Box 356, Seoul (KR).

(22) International Filing Date: 9 January 2003 (09.01.2003)

(81) Designated States (national): CN, JP, SG, US.

(25) Filing Language: English

(84) Designated States (regional): European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR).

(26) Publication Language: English

Published:

(30) Priority Data:
10-2002-0001773 11 January 2002 (11.01.2002) KR
10-2002-0053240 4 September 2002 (04.09.2002) KR

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

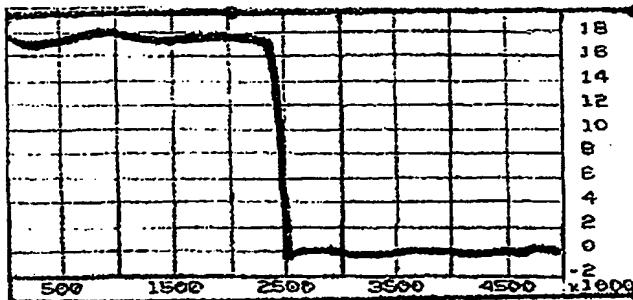
(71) Applicant (for all designated States except US): CLARI-ANT INTERNATIONAL LTD. [CH/CH]; Rothausstrasse 61, CH-4132 Muttenz 1 (CH).

[Continued on next page]

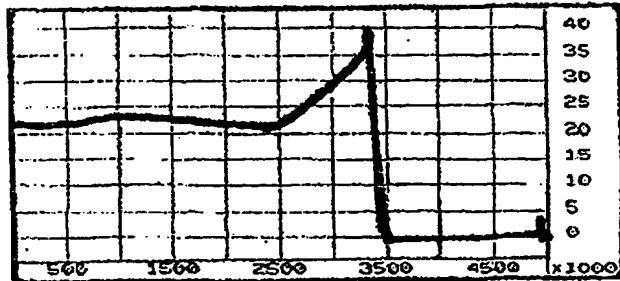
(72) Inventors; and

(75) Inventors/Applicants (for US only): OH, Sae-Tae

(54) Title: A CLEANING AGENT COMPOSITION FOR A POSITIVE OR A NEGATIVE PHOTORESIST



Composition of examples 1 and 2



Composition of comparative example 1

* X axis: Distance from the cleaned area (unit: 1nm).

* Y axis: Height of the photoresist coating (unit: 0.1μm)

(57) Abstract: The present invention relates to a composition for cleaning a photoresist and is to provide a cleaning composition wherein the residue of the photoresist does not remain on the boundary surface between the cleaned area and the not-cleaned area after a negative photoresist containing pigment is cleaned, soft-baked, exposed and developed. The present invention provides a composition for cleaning a positive or negative photoresist which comprises (a) from 0.1 to 20 wt.% of an alkyl oxide polymer with a molecular weight of from 50 to 2000 and (b) from 80 to 99.9 wt.% of an organic solvent comprising: (b-1) from 1 to 20 parts by weight of dipropylene glycol methyl ether (DPGME), from 10 to 50 parts by weight of N-methyl pyrrolidone (NMP) and from 50 to 90 parts by weight of methyl isobutyl ketone (MIBK), or (b-2) from 10 to 90 parts by weight of dimethyl formaldehyde (DMF) or dimethylacetamide (DMAc) and from 10 to 50 parts by weight of n-butyl acetate.

WO 03/058350 A1



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

DESCRIPTION

A cleaning agent composition for a positive or a negative photoresist

Technical Field

The present invention relates to a composition for cleaning a photoresist and, more specifically, to a composition for cleaning a photoresist which is useful for removing photosensitive material remaining on undesirable areas of the substrate for coating a photosensitive material and the instrument contacting the photosensitive material during processing of a fine circuit using a positive or negative photoresist composition and a negative photoresist composition containing pigment.

Background Art

It is well known in the art to produce photoresist compositions such as those described in US Patent Nos. 3,666,473, 4,115,128 and 4,173,470. These include phenol-formaldehyde novolak resins together with light-sensitive materials, usually a substituted naphthoquinone diazo compound.

The novolak resin component of those photoresist compositions is soluble in an alkaline aqueous solution, but the naphthoquinone diazo compound acts as a dissolution rate inhibitor with respect to the resin. Upon exposure of selected areas of the coated substrate to actinic radiation, however, the photoresist undergoes a radiation induced structural transformation and the exposed areas of the coating are rendered more soluble than the unexposed areas. The relief pattern of photoresist on substrate prepared by the process mentioned above is useful for providing $1\mu\text{m}$ very small line and

space widths, for example, in the manufacture of a semiconductor.

Further, in the process for preparing such very small circuits, the circuit density can be increased, using photolithography techniques, by increasing the resolution capabilities of the resist. Such photoresist has been widely used for preparing a semiconductor and a liquid crystal display device. In the liquid crystal display device, examples of using a photosensitive material during color filter process are described in more detail below.

In the color filter process, a positive photosensitive material of a negative photosensitive material containing pigment was coated on the glass or conductive metal film or layer having a rectangular pattern (hereinafter referred to as "substrate"), soft-baked, exposed and developed to prepare a pattern of the desired shape. In the course of forming such fine circuit pattern, when forming a photosensitive film on the substrate, the photoresist film formed at the edge of the substrate becomes irregular when compared with the photoresist film formed at the middle of the substrate. Further, the photosensitive material coated irregularly at the edge of the substrate during soft-baking or exposing process may lead to contamination by an accumulation of photosensitive material and thus, the removal thereof is required.

As the process for removing the coated photoresist layer by a physical process, a process for scraping the layer is known. However, such process has a problem in that the removal of the layer is not regular and the layer is damaged. As the process for stripping and cleaning the photoresist layer by a chemical process, the process for removing the photoresist layer with a chemical solution is known.

US Patent No. 4,983,490 discloses a solution for treating a photoresist film which comprises from 1 to 10 parts by weight of propylene glycol alkylether (PGME) and from 1 to 10 parts by weight of propylene glycol alkyl ether acetate (PGMEA), which exhibits excellent properties mainly in treating a positive photoresist, but it has disadvantages in treating a negative photoresist. The negative photoresist containing pigment is a photoresist used for a color filter of liquid crystal display devices. As such photoresist, black, red, blue and green photoresists may be used. When the photoresist containing pigment is cleaned with the cleaning composition consisting of from 1 to 10 parts by weight of PGME and from 1 to 10 parts by weight of PGMEA, the cleaning capability is lowered and a residue of the photoresist remains on the boundary surface between the cleaned area and the not-cleaned area of the developer after developing process.

Disclosure of Invention

The purpose of the present invention is to provide a cleaning composition wherein the residue of the photoresist does not remain on the boundary surface between the cleaned area and the not-cleaned area after a negative photoresist containing pigment is cleaned, soft-baked, exposed and developed.

Another purpose of the present invention is to provide a cleaning composition which does not produce a build-up property where the photoresist layer raises higher than the original coated thickness on the boundary surface between the area cleaned by the cleaning composition and the area not cleaned.

The further purpose of the present invention is to provide a photoresist layer

cleaning composition that has an excellent cleaning property.

In order to accomplish the purposes mentioned above, the present invention provides a cleaning composition which comprises (a) from 0.1 to 20 wt.% of an alkyl oxide polymer with a molecular weight of from 50 to 2000 and (b) from 80 to 99.9 wt.% of an organic solvent.

The organic solvent (b) preferably includes (b-1) a mixture of methyl isobutyl ketone (MIBK), dipropylene glycol methyl ether(DPGME) and N-methyl pyrrolidone(NMP), or (b-2) a mixture of dimethyl formamide(DMF) and n-butyl acetate, or (b-3) a mixture of dimethylacetamid(DMAc) and n-butyl acetate. Hereinafter, the present invention is described in detail.

The cleaning composition of the present invention comprises (a) an alkyl oxide polymer with a molecular weight of from 50 to 2000; and (b) organic solvent which contains (b-1) a mixture of methyl isobutyl ketone (MIBK), dipropylene glycol methyl ether(DPGME) and N-methyl pyrrolidone(NMP), or (b-2) a mixture of dimethyl formamide(DMF) and n-butyl acetate, or (b-3) a mixture of dimethylacetamide(DMAc) and n-butyl acetate.

The preferred amount of the alkyl oxide polymer(a) is from 0.1 to 20 wt.% with respect to the total amount of the composition. When the amount of the polymer exceeds 20 wt.%, it is not completely volatilized during soft-bake and thus, it is not preferable. When the amount is less than from 0.1 wt.%, the residual photosensitive material remains on the boundary surface between the cleaned area and the not-cleaned area after the coated photosensitive material is exposed to light and developed.

Further, even when the molecular weight of the polymer exceeds

2000, there is a problem in that it is not completely volatilized. When the molecular weight is less than 500, the residual photosensitive material remains on the boundary surface between the cleaned area and the not-cleaned area after the coated photosensitive material is exposed to light and developed. This is not preferable.

The most preferable alkyl oxide polymer is an ethylene or propylene oxide polymer, and even if any group is substituted on the two end groups of the alkyl oxide polymer, the performance does not change. The compositions of the organic solvent (b) suitable for mixing with the alkyl oxide polymer (a) are as follows:

(b-1) One example of the preferred organic solvent mixture is a mixture consisting of from 1 to 20 parts by weight of dipropylene glycol methyl ether (DPGME), from 10 to 50 parts by weight of N-methyl pyrrolidone (NMP) and 50 to 90 parts by weight of methyl isobutyl ketone (MIBK).

In the case of dipropylene glycol methyl ether (DPGME), when exceeding 20 parts by weight, it is not completely volatilized and thus it is not preferable. When the amount is less than 1 part by weight, the cleaning power is lowered and thus it is not preferable. In the case of the N-methyl pyrrolidone(NMP), when it is mixed in the amount of less than 10 parts by weight, the cleaning power is abruptly lowered and thus it is not preferable. Therefore, it is particularly preferable to mix NMP in the amount of up to 50 parts by weight. In the case of the methyl isobutyl ketone(MIBK), when it is mixed in the amount of less than 50 parts by weight, the cleaning power is lowered and thus it is not preferable. It is particularly preferable to mix MIBK in the amount of up to 90 parts by weight.

(b-2) The second example of the preferred organic solvent mixture is a mixture consisting of from 10 to 90 parts by weight of dimethyl formamide (DMF) and from 10 to 50 parts by weight of n-butyl acetate. When the amount of n-butyl acetate exceeds 50 parts by weight or is less than 10 parts by weight, there is a problem that the cleaning power is lowered.

(b-3) Another preferred organic solvent mixture is a mixture consisting of from 10 to 90 parts by weight of dimethylacetamide(DMAc) and from 10 to 50 parts by weight of n-butyl acetate. When the amount of n-butyl acetate exceeds 50 parts by weight or is less than 10 parts by weight, there is a problem that the cleaning power is lowered.

In case of the organic solvent (b-1), (b-2), and (b-3), the excellent property of not producing a build-up property where the coating thickness of the photoresist becomes thicker than the original coated thickness, upon cleaning of a positive photoresist, on the boundary surface between the cleaned area and the not- cleaned area of the photosensitive materials is achieved.

Brief Description of Drawings

Fig. 1 is a graph showing respective build-up properties when positive photoresist was cleaned with the cleaning composition of the present invention and with the cleaning agent of a conventional organic solvent.

Fig. 2 shows a residual of photoresist when a color photoresist was cleaned with the cleaning composition of the present invention.

Hereinafter, the present invention is more specifically described by way of

examples and comparative examples.

Example 1

The positive photoresist, AZ HKT501, was coated on a 370mm × 470mm glass substrate using a spinner. The photoresist layer was dissolved and removed from the peripheral area and the back area of the glass plate using a composition prepared by mixing 3 wt.% of alkyl oxide polymer having molecular weight of 300 with an organic solvent of 80 wt.% of DMF or DMAc and 17 wt.% of n-butyl acetate in DNS EBR apparatus. The results were observed by microscope and confirmed that no residual photoresist remained.

Example 2

The photoresist layer was dissolved and removed from the peripheral area and the back area of the glass plate using, as a removing solvent cleaning composition, a composition prepared by mixing 3 wt.% of alkyl oxide polymer having molecular weight of 300 with an organic solvent of 7 wt.% of DPGME, 20 wt.% of NMP and 70 wt.% of MIBK, instead of the solvent of Example 1. The results were observed by microscope and confirmed that no residual photoresist remained.

Comparative Example 1

An experiment was conducted in the same manner as Example 1 using, as the removing solvent, 30 wt.% of propylene glycol monomethyl ether acetate (PGMEA) and 70 wt.% of propylene glycol monomethyl ether(PGME). The build up was measured and the result is shown in Fig. 1.

Fig. 1 is a graph showing build up properties when the substrate is coated with the cleaning composition of the present invention prepared in Examples 1 and 2 and with the cleaning composition using the general organic solvent in Comparative Example 1, after the positive photoresist AZ HKT501 is coated on the substrate. As shown in Fig 2, the residual photosensitive material remains on the boundary surface between the cleaned area and the not-cleaned area after the coated photosensitive material is exposed to light and developed.

Fig. 2 is a photograph showing a residual of the photoresist when a color photosensitive agent is cleaned with the cleaning composition of the present invention prepared in Example 1 and 2. As shown in Fig. 2, JSR color photoresists (R, G, B) were coated on the substrate, washed with the cleaning composition of the present invention prepared in Examples 1 and 2, baked and developed. As a result, it can be confirmed that no residue of the photoresist remained.

Effect of Invention

As set forth above, the composition for cleaning the positive or negative photoresist has an excellent washing power since no residue remains after cleaning. The build up phenomenon is not produced on the boundary surface between the cleaned area and the not-cleaned area. There is no problem that the cleaning solution is immersed into the photoresist to change the coating thickness.

CLAIMS

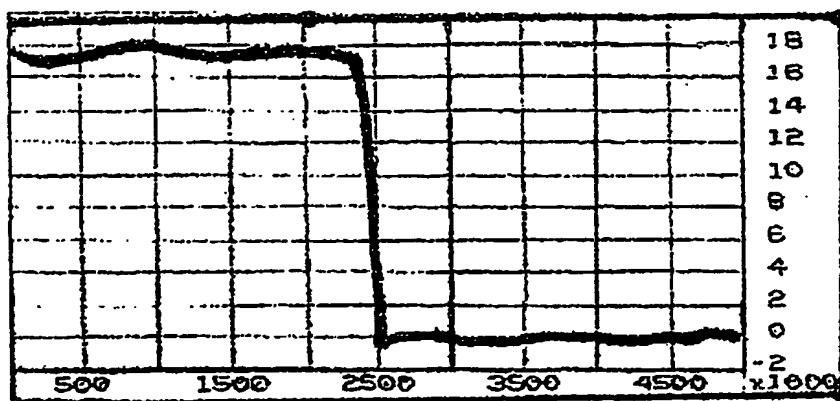
1. A composition for cleaning a positive or negative photoresist which comprises (a) from 0.1 to 20 wt.% of an alkyl oxide polymer with a molecular weight of from 50 to 2000; and (b) from 80 to 99.9 wt.% of an organic solvent containing from 1 to 20 parts by weight of dipropylene glycol alkyl ether (DPGAE), from 10 to 50 parts by weight of N-methyl pyrrolidone(NMP) and from 50 to 90 parts by weight of methyl isobutyl ketone (MIBK).
2. The composition for cleaning a positive or negative photosensitive material of claim 1, wherein the alkyl oxide polymer is ethylene oxide polymer.
3. The composition for cleaning a positive or negative photosensitive material of claim 1, wherein the alkyl oxide polymer is propylene oxide polymer.
4. The composition for cleaning a positive or negative photosensitive material of any one of claims 1 to 3, wherein the dipropylene glycol alkylether is dipropylene glycol methyl ether.
5. A composition for cleaning a positive or negative photoresist which comprises (a) from 0.1 to 20 wt.% of an alkyl oxide polymer with a molecular weight of from 50 to 2000; and (b) from 80 to 99.9 wt.% of an organic solvent containing from 10 to 90 parts by weight of dimethyl formamide (DMF) or dimethylacetamide (DMAc) and from 10 to 50 parts by weight of n-butyl acetate.

6. The composition for cleaning a positive or negative photosensitive material of claim 5, wherein the alkyl oxide polymer is ethylene oxide polymer.
7. The composition for cleaning a positive or negative photosensitive material of claim 5, wherein the alkyl oxide polymer is propylene oxide polymer.

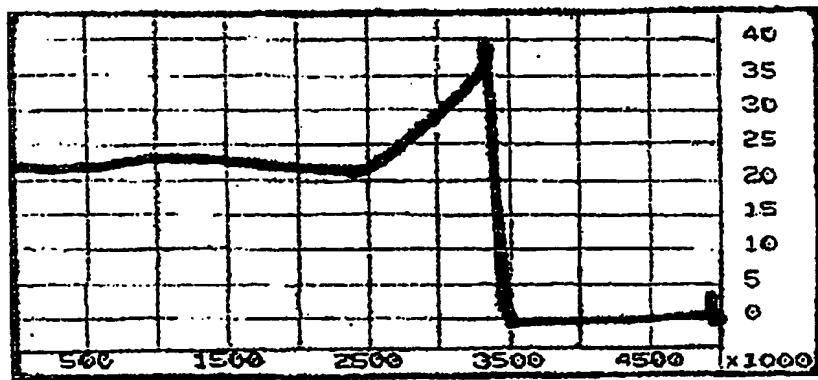
1/2

DRAWINGS

[Figure 1]



Composition of examples 1 and 2

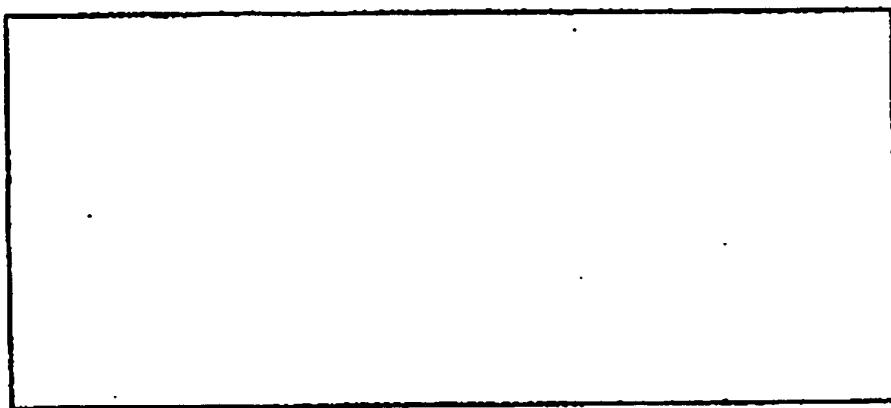


Composition of comparative example 1

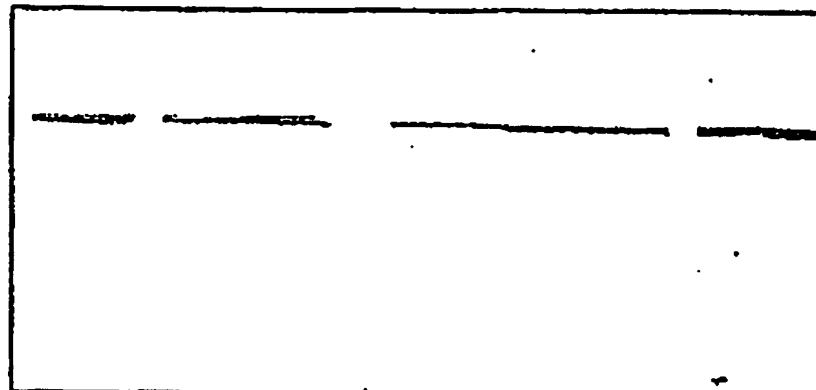
- * X axis: Distance from the cleaned area (unit: 1nm).
- * Y axis: Height of the photoresist coating (unit: 0.1μm)

2/2

[Figure 2]



Composition of examples 1 and 2



Composition of comparative example 1

INTERNATIONAL SEARCH REPORT

national application No.

PCT/KR03/00030

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 G03F 7/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 G03F 7/32, G03F 7/42, B08B 3/04, C11D 1/66, C09D 3/80, C09D 9/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
KR, JP: classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NPS, ESPACENET, DELPHION etc.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 65 381 A2 (Shuttleworth) 11.24.1982 see the whole document	1 - 7
A	EP 376 687 A2 (Global chemical systems INC) 04.07.1990 see the whole document	1 - 7
A .P	US 6,368,421 B1 (Joseph E. Oberlander etc.) 09 04.2002 see the whole document	1 - 7
A	US 5,288,335 A (Edwin Stevens) 22.02.1994 see the whole document	1 - 7
A	US 4,749,510 A (Henry J. Nelson) 07.06.1988 see the whole document	1 - 7
A	US 5,098,591 A (Edwin Stevens) 24.03.1992 see the whole document	1 - 7
A	JP 61-120866 A (DAINIPPON INK CHEMICAL) 07.06.1986 see the whole document	1 - 7

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search	Date of mailing of the international search report
28 MAY 2003 (28.05.2003)	28 MAY 2003 (28.05.2003)
Name and mailing address of the ISA/KR	Authorized officer
 Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	KIM, Hyun Sook Telephone No. 82-42-481-5584



INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR03/00030

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 65 381 A2	11.24.1982	AU 8328082 A1	02.02.1983
EP 376 687 A2	04.07.1990	DK 670989 A0 US 5030290 A	28.12.1989 30.06.1990
US 6,368,421 B1	09.04.2002	WO 003306 A1 CN 1308737 T EP 1097405 A1	20.01.2000 15.08.2001 09.05.2001
US 5,288,335 A	22.02.1994	NONE	
US 4,749,510 A	07.06.1988	CA 1322321A	21.09.1993
US 5,098,591 A	24.03.1992	NONE	
JP 61-120866 A	07.06.1986	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.